



The Accelerating Effect of Additives on Radiation-Induced Graft Polymerization

by

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Prepared for:

**THE OFFICE OF ISOTOPES DEVELOPMENT
United States Atomic Energy Commission**

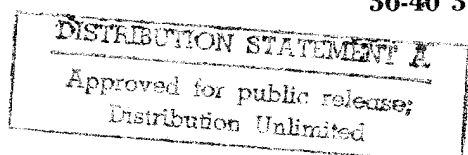
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FINAL REPORT

January 31, 1962

RADIATION APPLICATIONS INCORPORATED

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THE ACCELERATING EFFECT OF
ADDITIVES ON RADIATION-INDUCED
GRAFT POLYMERIZATION

This work performed for
The Division of Isotopes Development
United States Atomic Energy Commission
Contract No. AT(30-1)-2318

FINAL REPORT

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36-40 Radiation Applications Incorporated
37th Street, Long Island City 1, New York

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ABSTRACT

1. The Acceleration of Graft Polymerization by Solvent Additives

(27) During the course of the work on this contract, it was observed that the rates of various radiation-induced graft polymerizations would be substantially increased by dilution of the monomers with certain solvents. These large rate increases were shown to be a general feature of graft polymerization since they occurred in a wide variety of graft polymerization systems. Monomers studied were styrene, methyl acrylate and t-butylaminoethyl methacrylate; polymers included polyethylene, polypropylene, polyvinyl chloride, Teflon and nylon.]

An analysis of the kinetics of these irradiation-induced graft polymerizations were made in order to elucidate the mechanism of the solvent acceleration. The accelerations in the rates of graft polymerization were demonstrated to be due to two mechanisms. One is the incursion of a Trommsdorff effect due to the insolubilization of the growing graft polymer chains in the solvent-monomer medium. The other mechanism is the enhancement in the degree of accessibility of monomer to grafting sites within the polymer brought about by the greater ability of the solvent additive to swell the base polymer. The former mechanism is mainly responsible for the effects observed in the grafting of polyethylene, polypropylene, polyvinyl chloride and Teflon, while the latter mechanism is operative in the grafting of nylon.

The commercial significance of these results is that it opens up the possibility of making radiation-induced graft polymerization a practical as well as useful process due to the lower costs brought about by the use of this technique. It allows the synthesis of certain copolymers, such as those of nylon, which could not be made by standard copolymerization techniques. In addition, this technique extends the applicability of graft polymerization to radiation sensitive polymers such as polypropylene, polyvinyl chloride, polymethacrylates and Teflon.

2. Resin-Monomer Mixtures

Radiation-induced grafting via the technique of irradiation of resin-monomer mixtures has been investigated. Monomer and polymer were mixed above the melt point of the latter and some of the properties of the irradiated blends examined. Two specific monomer-polymer systems were studied with the following results:

a) Irradiated polyethylene-vinyl stearate mixtures showed increased plasticization.

b) Irradiated blends of polyethylene with diallyl phosphite and triallyl phosphate show improved temperature stability.

3. Publications

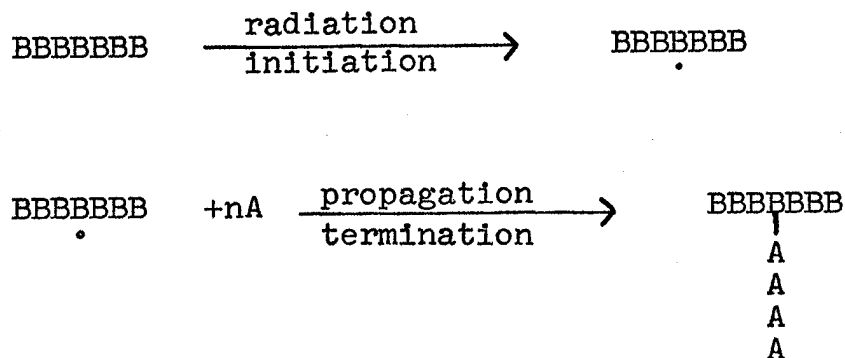
The following publications have resulted from the work performed under this project:

- a) G. Odian, A. Rossi, and E. N. Trachtenberg, "The Accelerating Effect of Methanol on the Gamma Radiation-Induced Graft Copolymerization of Styrene to Polyethylene," J. Polymer Sci., 42, 575 (1960).
- b) G. Odian, "Organic-Irradiation Yields," Nucleonics, 18, 185 (1960).
- c) G. Odian, M. Sobel, A. Rossi, and R. Klein, "Radiation-Induced Graft Polymerization : The Trommsdorff Effect of Methanol," J. Polymer Sci., 55, 663 (1961).
- d) G. Odian and H. W. Chandler, "Radiation-Induced Graft Polymerization," in "Advances in Nuclear Science and Engineering," Academic Press, in press (1962).
- e) G. Odian, M. Sobel, A. Rossi, R. Klein, and T. Acker, "Radiation-Induced Graft Polymerization of Styrene to Nylon," J. Polymer Sci., in press (1962).

1.0 INTRODUCTION

Investigations carried out under this contract have dealt with the study of radiation-induced graft polymerization. The modification and upgrading of polymeric materials by this reaction has received widespread and deserved interest. Graft polymerization is the process in which a monomer "A" is polymerized onto a polymer "B" in a manner such that the "A" polymer formed constitutes a "branch" on the "trunk" of the "B" polymer. The analogy to botanical grafting is obvious.

Although there are various methods for initiating the grafting reaction (peroxides, ultraviolet radiation, mastication, etc.), ionizing radiation is probably the most convenient and versatile. Irradiation of a polymer with atomic radiation is known to cleave chemical bonds homolytically, and the resulting free radicals are then capable of initiating a graft polymerization, i.e.,



Radiation-induced graft polymerization is a powerful means of incorporating into one polymer the unique properties of several polymers. By this technique it is possible to synthesize copolymers having almost any range of composition. It is even possible to synthesize copolymers that are a combination of a condensation and an addition polymer. An example is the graft copolymer of nylon and styrene that was investigated in detail under this contract. A detailed understanding of the reaction mechanism of graft polymerization should permit the synthesis of polymers having "tailor-made" properties.

2.0 SUMMARY

The investigations carried out under this contract have been concerned with the study of the effects of solvents on the process of radiation-induced graft polymerization. It has been found that the use of the proper solvent has a pronounced accelerative effect on the rate of grafting. A number of grafting systems have been investigated and despite polymer-monomer-solvent differences the accelerative effect was observed. This showed the effect to be a general phenomenon of graft polymerization. This work has shown two different mechanisms to be responsible for the accelerative effect. One is the Trommsdorff effect of the solvents and the other is the swelling effect of certain solvents on certain polymers.

The Trommsdorff effect is a phenomenon well known in homopolymerization and refers to the increased rate of polymerization that occurs during the later stages of the process when either the polymer precipitates or there is a large increase in viscosity. This accelerative effect, which is brought about by the physical state of the medium in which the polymerization takes place, has been ascribed to the fact that the large, growing polymer chains become immobilized and their rate of collision and hence termination becomes sharply decreased. However, the reactions of the monomer remain unaffected since this is a relatively small entity and does not lose its mobility. This decrease in termination rate, unaccompanied by a change in initiation rate, leads to

a higher steady state concentration of radicals and hence to a higher over-all rate of polymerization.

Since the rate of polymerization is proportional to monomer concentration unless monomer is available in sufficient concentration at the sites where polymerization occurs, the process will be inefficient. In this work it was shown that dilution of monomer with solvent can greatly increase the monomer concentration inside certain polymers and in this way yield an increased rate of graft polymerization.

The following grafting systems have been investigated and solvent acceleration has been found.

1. low density polyethylene-styrene-methanol
2. high density polyethylene-styrene-methanol
3. polypropylene-styrene-methanol
4. polyvinyl chloride-styrene-methanol
5. nylon-styrene-methanol
6. high density polyethylene-methyl acrylate-methanol
7. polypropylene-methyl acrylate-methanol
8. nylon-methyl acrylate-methanol
9. low density polyethylene-t-butylaminoethyl
methacrylate-hexane
10. Teflon-methyl acrylate-methanol

The magnitude of these accelerative effects differ for the various systems and can be seen in Table 2.1 below.

Table 2.1

The Accelerative Effect of Solvents on the Rate of Radiation-Induced Graft Polymerization

Grafting System	Irradiation dose rate in Mrads/hr.	Rate of grafting in % graft/Mrad
Polyethylene-low density		
styrene	0.070	61.4
styrene 50% (vol.) in methanol	0.070	117
t-butylaminoethyl methacrylate	0.020	305
t-butylaminoethyl methacrylate 70% (vol.) in n-hexane	0.020	1100
Polyethylene-high density		
styrene	0.081	127
styrene 50% (vol.) in methanol	0.081	414
methyl acrylate	0.061	82
methyl acrylate 30% (vol.) in methanol	0.061	124
Polypropylene		
styrene	0.080	84
styrene 50% (vol.) in methanol	0.080	319
methyl acrylate	0.021	119
methyl acrylate 50% (vol.) in methanol	0.021	134
Polyvinyl chloride		
styrene	0.041	negligible
styrene 30% (vol.) in methanol	0.041	337
Teflon		
methyl acrylate	0.061	41
methyl acrylate 30% (vol.) in methanol	0.061	93.5
Nylon		
styrene	0.071	negligible
styrene 50% (vol.) in methanol	0.071	200
methyl acrylate	0.070	negligible
methyl acrylate 50% (vol.) in methanol	0.070	176

For any grafting system although both the Trommsdorff and the solvent swelling effect can be operative in leading to acceleration in the rate of graft polymerization, usually one of these predominates.

The Trommsdorff effect has been shown to predominate in the grafting of styrene, methyl acrylate and t-butylaminoethyl methacrylate to polyethylene, polypropylene, polyvinyl chloride and Teflon. Solvent swelling has been shown to be the effect mainly responsible for the acceleration in the grafting of styrene and methyl acrylate to nylon.

3.0 SIGNIFICANCE OF THIS WORK

This study of the effects of solvent additives on radiation-induced graft polymerization has shown that the rate of this process can be substantially increased by monomer dilution with the proper solvent. Many important industrial implications ensue because of the discovery of this strong accelerative effect. This investigation has shown the effect to be a general phenomenon of the process and widely applicable to many different systems.

This effect is important because it opens up new fields for the application of graft polymers synthesized by radiation. The radiation doses and costs necessary to produce graft polymers are drastically reduced. Substitution of a non-consumed, inexpensive component, the solvent, for monomer leads to lowered monomer expenses. The production of graft polymers from radiation sensitive polymers and monomers now becomes a feasible operation. It must be emphasized that many of the new and interesting products that can be made by radiation-induced graft polymerization would not be obtainable by other copolymerization techniques. The case of the graft polymers of nylon which were studied in detail under this contract are an example of this type.

Since this study has pointed out the causes for the solvent acceleration effect, it therefore becomes possible

to predict beforehand the additives that would be effective for use in projected graft polymerization systems. With solvent acceleration as a tool it becomes possible to design and carry out the synthesis of a wide variety of "tailor-made" graft polymers with radiation by a convenient, practical and efficient method.

4.0 THE ENHANCEMENT OF THE RATE OF GRAFT POLYMERIZATION
BY SOLVENT ADDITIVES

4.1 The Graft Polymerization of Styrene

It has been found that the rate of the graft polymerization of styrene to the base polymers low density polyethylene, high density polyethylene, polypropylene, polyvinyl chloride and nylon was substantially increased when the styrene monomer was diluted with methanol. The effect of methanol on the initial grafting rates of styrene to the various polymers can be seen in Tables 4.1 - 4.5. All graft polymerizations were carried out at 25°C.

Table 4.1

Effect of Methanol on the Grafting of Styrene to Low Density Polyethylene^a

Vol. % styrene in outside solution	% Graft/hr.
100	4.3
90	7.1
70	6.9
50	8.2
30	11.9
10	6.1

^a Dose rate = 0.070 Mrads/hr.

Table 4.2

Effect of Methanol on the Grafting of Styrene to High Density Polyethylene^a

Vol. % styrene in outside solution	% Graft/hr.
100	10.3
90	19.5
70	22.5
50	33.5
30	14.3
10	1.7

^a Dose rate = 0.081 Mrads/hr.

Table 4.3

Effect of Methanol on the Grafting of Styrene to Polypropylene^a

Vol. % styrene in outside solution	% Graft/hr.
100	6.7
90	10.2
70	10.5
50	25.5
30	2.4
10	1.0

^a Dose rate = 0.080 Mrads/hr.

Table 4.4

Effect of Methanol on the Grafting of Styrene to Polyvinyl Chloride^a

Vol. % styrene in outside solution	% Graft/hr.
100	0
70	2.4
50	5.4
30	13.8

^a Dose rate = 0.041 Mrads/hr.

Table 4.5

Effect of Methanol on the Grafting of Styrene to Nylon^a

Vol. % styrene in outside solution	% Graft/hr.
100	0.0
90	17.8
70	16.6
50	14.2
30	11.8
10	4.9

^a Dose rate = 0.071 Mrads/hr.

For the graft polymerization of styrene with polyethylene (low and high density), polypropylene and polyvinyl chloride the mechanism for the increased rates observed on dilution of the styrene with methanol was attributed to the incursion of a Trommsdorff effect brought about because of the insolubility of polystyrene in methanol. Differences among the styrene grafting rates for the various polymers studied were attributed to variations in density, crystallinity and in G value of the polymers.

Prior to this work it had been noted that the radiation-induced graft polymerization of styrene to nylon was a very inefficient reaction. Ballantine and co-workers¹ obtained a 10.5% graft of styrene to nylon with a radiation dose of 31.1 Mrads. Any industrial application of the grafting operation was economically unfeasible due to the high radiation dose requirements. The observations in this laboratory showed that dilution of styrene with methanol led to enhanced access of the monomer to the grafting sites in the nylon and this in turn produced a greatly enhanced grafting rate. By using this technique of solvent acceleration it became possible to accomplish the graft polymerization of styrene to nylon in a feasible and economical manner.

4.2 The Graft Polymerization of Acrylates

The rates of the radiation-induced graft polymerizations of the polar, functional monomers, methyl acrylate and t-butylaminoethyl methacrylate, were shown also to be sensitive to the effect of solvent additives. Acceleration in the rates of grafting of methyl acrylate to high density polyethylene, polypropylene, nylon and TFE Teflon were obtained when the monomer was diluted with methanol. The rate of the graft polymerization of t-butylaminoethyl methacrylate to low density polyethylene was shown to be increased by the use of hexane. This demonstrated that it was possible to use solvent additives to increase the rates of graft polymerization of polar monomers (the acrylates) as well as a non-polar monomer (styrene). The effect of solvent dilution on the rates of graft polymerization of the acrylates can be seen below in Tables 4.6 - 4.10. All graft polymerizations were carried out at 25°C.

Table 4.6

Effect of Methanol on the Grafting of Methyl Acrylate to High Density Polyethylene^a

Vol. % methyl acrylate in outside solution	% Graft/hr.
100	5.1
90	4.8
70	4.3
50	4.8
30	7.6
10	1.4

^a Dose rate = 0.061 Mrads/hr.

Table 4.7

Effect of Methanol on the Grafting of Methyl Acrylate to Polypropylene^a

Vol. % methyl acrylate in outside solution	% Graft/hr.
100	2.5
90	1.6
70	1.8
50	2.8
30	1.8

^a Dose rate = 0.021 Mrads/hr.

Table 4.8

Effect of Methanol on the Grafting of Methyl Acrylate to Nylon^a

Vol. % methyl acrylate in outside solution	% Graft/hr.
100	0.47
90	6.9
70	16.9
50	12.3
30	7.6

^a Dose rate = 0.070 Mrads/hr.

The acceleration in the rates of graft polymerization of methyl acrylate to high density polyethylene, polypropylene and TFE Teflon that occurred on dilution of the monomer with methanol were caused by the onset of a Trommsdorff effect. This effect was also responsible for the increase in the rate of the graft polymerization of t-butylaminoethyl methacrylate to low density polyethylene that came about when the monomer was diluted with hexane.

Table 4.9

Effect of Methanol on the Grafting of Methyl Acrylate to Teflon^a

Vol. % methyl acrylate in outside solution	% Graft/hr.
100	2.5
90	2.3
70	2.1
50	2.3
30	5.8

^a Dose rate = 0.61 Mrads/hr.

Table 4.10

Effect of n-Hexane on the Grafting of t-Butylaminoethyl Methacrylate to Low Density Polyethylene^a

Vol. % t-baem. in outside solution	% Graft/hr.
100	6.1
90	10.3
70	22.0
50	14.5

^a Dose rate = 0.020 Mrads/hr.

The grafting of methyl acrylate to nylon with methanol was an interesting case. In this system the acceleration in the rate of graft polymerization on the addition of solvent was caused by both the onset of the Trommsdorff effect and the effect of solvent swelling on the polymer.

4.3 Experimental

4.3.1 Materials

The low density polyethylene was Du Pont B301 3 mil film. The high density polyethylene was Union Carbide Visotherm 3 mil film. The polypropylene was Avisun 5 mil film. The TFE Teflon was Du Pont 3 mil film. The polyvinyl chloride was Bakelite QBAA-6304 1.5 mil cast film.

Styrene, stabilized, was washed with 10% sodium hydroxide, dried twice over magnesium sulfate and distilled through a Vigreux column Bp. $45^{\circ}\text{C.}/15\text{ mm.}$ Methyl acrylate, Rohm and Haas, inhibited, was washed with a 5% sodium hydroxide-20% sodium chloride solution, dried over magnesium and calcium sulfate and distilled using a Vigreux column, Bp. $44^{\circ}\text{C.}/210\text{ mm.}$ t-Butylaminoethyl methacrylate, Rohm and Haas, inhibited with N,N'-diphenyl-p-phenylene diamine, was distilled through a Vigreux column, Bp. $52^{\circ}\text{C.}/3\text{ mm.}$

Methanol was dried over soda lime and then distilled. n-Octane was dried over magnesium sulfate and distilled. Reagent grade n-hexane was distilled before use.

4.3.2 Graft Polymerization Procedure

All the polymer films were washed in benzene and then dried under vacuum at 65°C. except the nylon which was dried at 85°C. The monomer-solvent solutions were made up by weight, the polymer films added and the mixtures purged with nitrogen at room temperature for 15 minutes except the t-butylaminoethyl methacrylate which was nitrogen purged at -20°C. for 20 minutes. The mixtures were then equilibrated overnight. All experiments were carried out in ground glass stoppered test tubes. Irradiations were carried out with the RAI Co-60 source facility. To avoid post-irradiation effects, samples were worked up as soon as possible. To remove homopolymer and monomer the films were washed with solvent for a number of hours. The styrene with benzene, the methyl acrylate with ethyl acetate and the t-butylaminoethyl methacrylate with acetone. The films were then dried as above under vacuum. The amount of graft was calculated as:

$$\text{percent graft} = \frac{\text{increase in wt.} \times 100}{\text{original wt. of polymer}}$$

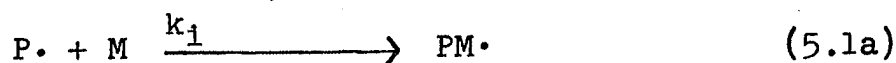
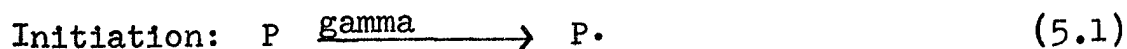
All grafting experiments were run in duplicate. With the styrene systems the reproducibility was very good, being of the order of $\pm 5\%$ in the majority of experiments. The precision of duplicate acrylate experiments was lower; agreement being in many cases no better than to within $\pm 15\text{-}20\%$. For styrene the rates of graft polymerization calculated were the initial rates. For acrylate, due to

the lower reproducibility, the rate curves were not good. Only qualitative significance should therefore be ascribed to most of the acrylate data. The scatter in duplicate grafting experiments with the acrylates was most probably due to small amounts of inhibitor and oxygen and these monomers were more sensitive than styrene.

5.0 THE MECHANISM OF THE ACCELERATION OF RADIATION-INDUCED GRAFT POLYMERIZATION WITH SOLVENT ADDITIVES

5.1 Derivation of Kinetic Equations

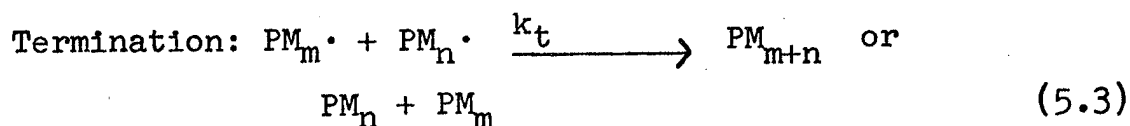
It was necessary to consider the kinetics of graft polymerization in order to elucidate the mechanism of the grafting process. By using a treatment similar to that in homogeneous homopolymerization² and a simplified kinetic scheme, the following series of equations for the various steps in a graft polymerization reaction may be written



$$R_1 = k_1(P\cdot)(M) \quad (5.1b)$$



$$R_p = k_p(PM_n\cdot)(M) \quad (5.2a)$$



$$R_t = 2k_t(PM_n\cdot)^2 \quad (5.3a)$$

where P represents the polymer chain, $P\cdot$ the polymer radicals, M the monomer, $PM_n\cdot$, $PM_{n+1}\cdot$, $PM_m\cdot$ the graft copolymer radicals, k_p and k_t the rate constants for propagation and bimolecular termination, respectively. (Concentrations are denoted by parentheses in the equations above and those throughout this report.)

For a long-chain process yielding high polymer, the rate of graft polymerization is given by equation 5.2a. The rate of change of concentration of graft copolymer radicals

may be written as

$$d(PM_n \cdot)/dt = k_i(P \cdot)(M) - 2k_t(PM_n \cdot)^2 \quad (5.4)$$

By introducing the conventional steady-state assumption that the rate of change of the concentration of $PM_n \cdot$ is small compared to its rates of formation and disappearance one obtains

$$(PM_n \cdot) = (R_i/2k_t)^{0.5} \quad (5.5)$$

Combining equations 5.2a and 5.5 yield for the rate of graft polymerization

$$R_p = k_p(M)(R_i/2k_t)^{0.5} \quad (5.6)$$

5.2 The Effect of Film Thickness on the Rate of Graft Polymerization

In order to define and assign values to the terms in equation 5.6 it was necessary to know whether the grafting reactions studied occurred volumetrically throughout the entire polymer or only on the surface.

Also, it was possible that the nature of the grafts was not the same when monomer-solvent was employed as when monomer was used alone. The experimental procedure employed was such that the grafts synthesized employing undiluted monomer were mainly volumetric or homogeneous grafts. The grafts synthesized using monomer-solvent solutions might consist largely of surface grafts. In other words, the accelerative effect of the solvent might be exerting itself

by resulting in an extra amount of monomer grafted to the surface of the backbone polymer. To elucidate the nature of the grafts in the two cases (undiluted monomer vs. monomer diluted with solvent), grafting experiments were performed using different thicknesses of film.

The grafting system low density polyethylene-30% styrene-70% methanol was studied employing 3 and 5 mil polyethylene films. Both thicknesses of film contained the same relative amounts of crystalline and amorphous polyethylene. These results are shown in Table 5.1 and 5.2. As can be seen from these results, the grafting rates (where grafts are expressed in grams of grafted polystyrene per gram of polyethylene) were independent of film thickness for both undiluted styrene and for the 70% methanol-30% styrene solution. If the accelerative effect of the methanol were simply a surface phenomenon, one would expect the 3 and 5 mil films to have the same grafting rates in undiluted styrene but different rates in methanol-styrene solution. In particular the 5 mil film would be expected to have a lower rate of grafting than the 3 mil film. Thus, the results showed that the grafts produced in all cases were volumetric grafts and that the accelerative effect of the methanol takes place homogeneously throughout the bulk of the polyethylene.

The effect of film thickness on the rate of grafting with the system nylon-50% styrene-50% methanol was also studied. Nylon films of 2,3 and 5 mil thickness were employed. The results of this study also showed the grafting reaction to be occurring volumetrically both in the case of pure monomer and monomer diluted with solvent.

Table 5.1

Effect of Film Thickness on the Grafting of Styrene-Methanol (30-70 vol. %) to Low Density Polyethylene^a

Thickness of film	Rate of grafting, % graft/hr.
3 mil	7.2
5 mil	7.5

^a Dose rate = 0.061 Mrads/hr.

Table 5.2

Effect of Film Thickness on the Grafting of Styrene to Low Density Polyethylene^a

Thickness of film	Rate of grafting, % graft/hr.
3 mil	4.1
5 mil	4.2

^a Dose rate = 0.061 Mrads/hr.

Since it was shown that the graft polymerization was a volumetric reaction which occurred homogeneously throughout the volume of the polymer, the various terms in equation 5.6 are defined in the following manner:

R_p = moles of monomer graft polymerized per liter of (monomer-solvent-amorphous polymer) per second

(M) = moles of monomer absorbed per liter of (monomer-solvent-amorphous polymer)

R_1 = moles of free radicals produced on amorphous polymer chains per liter of (monomer-solvent-amorphous polymer) per second

k_p = rate constant of propagation

k_t = rate constant of termination

5.3 The Effect of n-Octane on the Graft Polymerization of Styrene to Polyethylene.

The observed enhanced rate in the graft polymerization of styrene to polyethylene was attributed to the incursion of a Trommsdorff effect brought about by the immobilization of the growing polystyrene graft polymer chains in the methanol. In order to verify this conclusion, n-octane was substituted for methanol as the solvent diluent.

n-Octane is quite similar to methanol in its radiation stability³ and viscosity properties,⁴ but the two solvents are quite different in their solvent properties toward polystyrene. Whereas polystyrene is insoluble in methanol, it is quite soluble in n-octane and therefore growing polystyrene chains in a n-octane-styrene medium would not become

immobilized or curled up as they would in a methanol-styrene medium. In proof of this, as can be seen in Tables 5.3 and 5.4, no accelerating phenomenon was found for the graft polymerization of n-octane-styrene solutions with low and high density polyethylene.

Table 5.3

Effect of n-Octane on the Grafting of Styrene to Low Density Polyethylene^a

Vol. % styrene in outside solution	% Graft/hr.
100	4.6
90	3.9
70	2.4
50	1.6
30	0.3

^a Dose rate = 0.068 Mrads/hr.

Table 5.4

Effect of n-Octane on the Grafting of Styrene to High Density Polyethylene^a

Vol. % styrene in outside solution	% Graft/hr.
100	11.8
90	10.9
70	6.1
50	3.7
30	1.3

^a Dose rate = 0.081 Mrads/hr.

5.4 The Effect of Radiation Intensity on the Graft Polymerization of Styrene with Nylon

The derivation of equation 5.6 assumed that termination of the grafting reaction was bimolecular. Although this is the usual situation in homopolymerization, one might speculate that the mode of termination in the grafting reaction might be monomolecular due to radical burial. These two modes of termination may easily be differentiated by a determination of the order of dependence of the graft polymerization rate on radiation intensity. Bimolecular termination would result in a one-half order dependence of R_p on intensity as indicated in equation 5.6 while monomolecular termination would result in a first power dependence.

Investigation was undertaken to determine whether this 0.5 order dependency held for the nylon-styrene-methanol grafting system. This was done by studying the graft polymerization reaction for the 50% styrene-50% methanol solution and 3 mil nylon film at three different dose rates. The plot of the initial rates of grafting vs. dose rate on a log-log graph yielded a straight line of slope 0.47, which within experimental error was 0.50. This showed that in the graft polymerization of styrene to nylon in the presence of methanol, termination is bimolecular.

5.5 The Calculation of k_p^2/k_t

In order to elucidate the mechanism of the acceleration caused by solvents in graft polymerization, the k_p^2/k_t values for the various grafting systems were determined. The ratio k_p^2/k_t was determined by employing equation 5.7 which is a rearranged form of equation 5.6

$$k_p^2/k_t = 2R_p^2/(M)^2R_1 \quad (5.7)$$

Since it had been shown that graft polymerization took place volumetrically throughout the base polymer, it was necessary to use the concentrations of monomer, (M), inside the polymer in order to calculate k_p^2/k_t . Therefore, the phase equilibria for the various polymer-monomer-solvent systems were determined and the monomer-solvent concentrations inside the base polymers calculated for the different grafting systems.

These phase equilibria were determined by equilibrating the polymer-monomer-solvent systems at 25°C. The polymers swollen with the equilibrium amounts of monomer and solvent were then subjected to gamma rays from the Co-60 source or electrons from a machine accelerator. This polymerized the monomer and rendered it non-volatile. The solvent could then be removed by vacuum drying. From the weight differences the amounts of monomer and solvent could be obtained separately.

The calculations of the kinetic parameters were made based on the assumption that 1) only the amorphous regions of the polymer were swollen by the monomer and solvent, 2) the grafting reaction took place only in the amorphous regions of the polymer, 3) the system amorphous polymer-monomer-solvent behaved like an ideal solution in that the individual volumes were additive.

The determination of the phase equilibria involved finding small differences and in order to avoid the possibility of introducing large errors all experiments were run in duplicate and most of them were repeated. The calculated values of monomer concentration and the kinetic parameters represent the average of four determinations. As there was good precision and reproducibility, it showed the method was reliable in indicating the order of magnitude of the calculated values, and as will be demonstrated, only qualitative significance can be ascribed to these values of k_p^2/k_t for the various graft polymerizations.

The rate of initiation of the graft polymerization reaction, R_i , is given by the equation

$$R_i = G\phi\rho / (6.023 \times 10^{25}) \quad (5.8)$$

where G = number of free radicals produced on amorphous polymer chains per 100 ev. of radiation energy absorbed

ϕ = radiation intensity in ev. absorbed per gram of amorphous polymer per second

ρ = grams of amorphous polymer per liter of (monomer-solvent-amorphous polymer)

The G value of 7 was assumed for polyethylene radical production. This G value was chosen since the corresponding G value for cyclohexane was approximately 7.⁵ A G value of 6.9 was used for polypropylene as this was the G value for 2-methylpentane.⁶ A G value of 5.8 was used for nylon radical production.⁷ The rates of polymerization, R_p , were calculated from the observed rates of grafting (Section 4.0). The calculated values of monomer concentration, (M), and the ratio k_p^2/k_t for the various grafting systems are shown in Tables 5.5 - 5.12. All of the data pertains to 25°C.

Table 5.5

Kinetic Parameters for the Grafting System Low Density
Polyethylene-Styrene-Methanol

Vol. % styrene in outside solution	(M)	k_p^2/k_t
100	2.0	0.12
90	1.8	0.41
70	1.6	0.53
50	1.4	1.0
30	0.98	4.5
10	0.38	8.3

Table 5.6

Kinetic Parameters for the Grafting System Low Density
Polyethylene-Styrene-Octane

Vol. % styrene in outside solution	(M)	k_p^2/k_t
70	1.3	0.091
50	1.0	0.063

Table 5.7

Kinetic Parameters for the Grafting System Low Density
Polyethylene-t-Butylaminoethyl Methacrylate-Hexane

Vol. % t-baem. in outside solution	(M)	k_p^2/k_t
100	0.32	15.5
90	0.29	25.6
70	0.24	278
50	0.18	197

Table 5.8

Kinetic Parameters for the Grafting System High Density
Polyethylene-Styrene-Methanol

Vol. % styrene in outside solution	(M)	k_p^2/k_t
100	1.7	4.4
90	1.5	21
70	1.4	32
50	1.2	94
30	0.87	35
10	0.36	3.1

Table 5.9

Kinetic Parameters for the Grafting System High Density
Polyethylene-Styrene-Octane

Vol. % styrene in outside solution	(M)	k_p^2/k_t
70	1.2	2.9
50	0.97	0.16

Table 5.10

Kinetic Parameters for the Grafting System Polypropylene-Styrene-Methanol

Vol. % styrene in outside solution	(M)	k_p^2/k_t
100	1.7	0.86
90	1.6	2.4
70	1.5	3.0
50	1.3	23
30	0.99	0.36

Table 5.11

Kinetic Parameters for the Grafting System Nylon-Styrene-Methanol

Vol. % styrene in outside solution	(M)	k_p^2/k_t
100	0.05	0
90	0.61	27
70	0.60	26
50	0.57	20
30	0.44	25
10	0.18	28

Table 5.12

Kinetic Parameters for the Grafting System Nylon-Methyl Acrylate-Methanol

Vol. % acrylate in outside solution	(M)	k_p^2/k_t
70	0.68	35
50	0.55	26
30	0.38	21

From an examination of the values of (M) , the concentration of the monomer inside the polymer, and the values of k_p^2/k_t (Tables 5.5 - 5.10), it can be seen that with both types of polyethylene and polypropylene, although the concentration of the monomer in the inside solution decreased as the concentration of monomer in the outside solution decreased, the k_p^2/k_t values went through a maximum or increased. Therefore, with these polymers the enhanced rate of the graft polymerization by monomer dilution was due to the onset of a Trommsdorff effect brought about by the insolubilization of the growing graft polymer chains in the solvent medium.

An examination of the (M) and k_p^2/k_t values for nylon (Tables 5.11 - 5.12) showed that dilution of the monomer with solvent led to large increases in the monomer concentration inside the polymer accompanied by an increase in the rate of polymerization. This increase in monomer concentration was mainly responsible for the increase in the grafting rate and was brought about because the nylon was swollen to a greater extent by monomer-solvent than by monomer alone.

A comparison of the k_p^2/k_t values for the graft polymerization of styrene to the corresponding value of 1.0×10^{-4} liter/mole/sec for the homopolymerization of styrene⁸ showed that the graft polymerization values were orders of magnitude larger. This also occurred with methyl acrylate whose k_p^2/k_t homopolymerization value is 0.64.⁹

Here too the graft polymerization values were several orders of magnitude larger. Although the k_p^2/k_t value for the homopolymerization of t-butylaminoethyl methacrylate is not known it is reasonable to expect that here too the graft polymerization k_p^2/k_t values are much larger. This increase in k_p^2/k_t has also been observed in the grafting of methyl methacrylate to rubber.¹⁰ Despite monomer and polymer differences, in all the grafting systems studied, this large increase in the k_p^2/k_t value was found. It was, therefore, concluded that this is a general phenomenon of graft polymerization.

This increase in k_p^2/k_t is due, no doubt, to the greater viscosity of the medium in which the grafting reaction took place. It is similar to the autoacceleration observed in the later stages of many homopolymerizations. Thus, a Trommsdorff effect is present in the grafting reaction even in the case of undiluted monomer. A further Trommsdorff effect is experienced when the monomer is diluted with solvent. This leads to further increases in the k_p^2/k_t value (see Tables 5.5 - 5.12). This latter Trommsdorff effect is due to an insolubilization of the graft polymer chains, whereas that observed in comparing graft and homopolymerization is due to the viscosity increase.

5.6 The Applicability of Steady State Conditions to Radiation-Induced Graft Polymerization

The derivation above of equation 5.6 assumed steady-state conditions with regard to polymer radicals. However, this may not be a valid assumption in view of the greatly increased

values of k_p^2/k_t . A cursory examination of the situation might lead one to postulate that because the findings of various workers show the existence of long lived radicals¹¹ from the irradiation of polyethylene and other polymers, any semblance of a steady state situation in the grafting reaction would be impossible. However, under the experimental conditions employed in this investigation, mutual irradiation of polymer and monomer, only the lifetime of radicals formed in the amorphous regions of the polymer in the presence of monomer affect the situation. The existing data on the lifetime of radicals in irradiated polymers in the absence of monomer is therefore not directly applicable to this situation.

Let us consider the kinetic equations which are applicable for the extreme case of non steady-state graft polymerization.

Integration of equation 5.4 yields

$$\int_0^{(PM_n \cdot)} \frac{d(PM_n \cdot)}{R_1 - 2k_t(PM_n \cdot)^2} = \int_0^t dt \quad (5.9)$$

$$(PM_n \cdot) = (R_1/2k_t)^{0.5} A \quad (5.10)$$

$$\text{where } A = \frac{e^{bt} - 1}{e^{bt} + 1} \quad (5.11)$$

$$b = 2(2k_t R_1)^{0.5} \quad (5.12)$$

Combining equations 5.2a and 5.17 yields

$$R_p = k_p(M)(R_1/2k_t)^{0.5} A \quad (5.13)$$

It is apparent that equation 5.13 would be essentially equivalent to equation 5.6 when A has a value close to unity. It would be possible to determine the error, if any, involved in the assumption of steady state conditions and the use of equation 5.6 by determining the value of A under the experimental conditions of radiation-induced graft polymerization.

In order to determine A and calculate the time needed to reach the steady state it was necessary to know k_p , the absolute rate constant for chain propagation. For homopolymerization the classical method employed to determine k_p is the rotating sector.¹² Adapting this technique to radiation initiated polymerizations would be extremely cumbersome. Therefore, an attempt was made to ascertain k_p from the rate of post-irradiation graft polymerization after two different mutual irradiation periods with the grafting system nylon-styrene-methanol. If steady state conditions prevail, the radical concentration would reach a constant value in a time interval much smaller than the total time of the grafting reaction. If the rate of post-irradiation polymerization after two different mutual irradiation times were found to be the same then it could be concluded that steady state conditions do indeed exist under the reaction conditions. From the determination of the rate of post-irradiation polymerization it would then be possible to calculate¹³ the value of k_p for the grafting reaction.

Since the ratio k_p^2/k_t for the nylon-styrene-methanol system was known (see Table 5.11), if k_p could be determined,

it would be possible to calculate k_t and the time necessary to reach steady state conditions in the graft polymerization.

Attempts to determine the rate of post-irradiation graft polymerization of the nylon-styrene-methanol system were unsuccessful. Some post-irradiation graft polymerization could be detected. The increments in the amount of graft per time interval were widely scattered, probably due to small amounts of oxygen present in the system. As the data could not be used for calculation, the value of k_p in this graft polymerization was not determinable and the evaluation of A not possible. It was possible, however, to make various calculations based on certain assumed values of k_p .

If it is assumed that the k_p value for the graft polymerization of styrene is the same as that for its homopolymerization ($k_p = 55$ liters/mole/second),¹⁴ A may be calculated to have a value of approximately 0.95 at $t = 300$ seconds and of 1.00 at $t = 600$ seconds. Under these conditions equation 5.6 could be employed with negligible error for calculating values of k_p^2/k_t if only data after $t = 300$ seconds is used.

However, it would seem unlikely that k_p remains unchanged in view of the very large change in k_p^2/k_t . If k_p in the grafting reaction had decreased to one-tenth of its value in homopolymerization, then A would have a value of 0.32 at $t = 600$ seconds, while if k_p has decreased to one-hundredth of its value, A would have a value of only

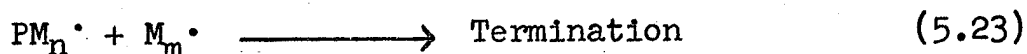
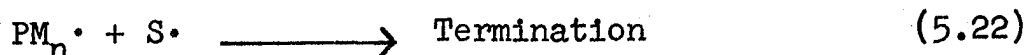
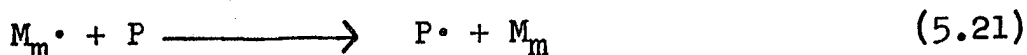
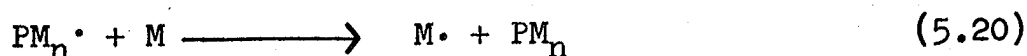
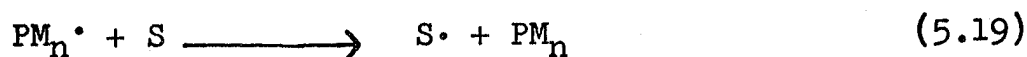
0.035 at $t = 600$ seconds. Under these conditions, especially the latter, appreciable errors would ensue in the use of equation 5.6 due to inapplicability of the steady state assumption.

It had been shown quite conclusively that the k_p^2/k_t values for graft polymerization are increased by order of magnitude relative to the value in homopolymerization. However, only qualitative significance should be ascribed to these k_p^2/k_t values since equation 5.6 which may not be strictly applicable was used for their calculation. Their validation as quantitative values awaits an actual determination of k_p for these grafting systems. One last point that is apparent is that for the graft polymerization of styrene, even if $k_p = 55$ (i.e., k_p is unchanged in grafting compared to homopolymerization), the time after the start of irradiation needed to attain or approach to within 95% of the steady state situation is much longer than is required in the corresponding homopolymerization of styrene.

5.7 An Analysis of the Kinetics of Graft Polymerization

The kinetic scheme employed to derive equation 5.6 was a simple one, as mentioned earlier, and did not take into account any of the following possible reactions





where S represents the solvent, M the monomer, $S \cdot$ the solvent radicals, $M \cdot$ the monomer radicals and $M_m \cdot$ the homopolymer radicals.

Let us consider the nylon-styrene-methanol grafting system. The extent to which chain transfer reactions 5.17 - 5.21 occur in this system may be ascertained by a consideration of the pertinent chain transfer constants. Primary alcohols are poor chain transfer agents. The transfer constant of n-butanol, for example, at 60°C., is 6×10^{-6} toward styryl radicals¹⁵ and 2.5×10^{-5} toward methyl methacrylate radicals.¹⁶ Thus, chain transfer from polyamide and graft copolymer radicals to methanol, reactions 5.17 and 5.19, would not be expected to be important in this system. Chain transfer from polyamide and graft copolymer radicals to styrene monomer, reactions 5.18 and 5.26, would also be expected to be nil based on the reported value¹⁷ of 6×10^{-5} for the self-transfer constant of styrene at 60°C. Chain transfer constants for amides are not available. However, those for comparable compounds¹⁵ such as propionic acid ($C = 5 \times 10^{-6}$) and diethyl malonate ($C = 4.7 \times 10^{-5}$) indicate that chain transfer from styrene homopolymer radicals to polyamide chains, reaction 5.21 would probably not occur to any appreciable extent.

At first glance it might appear that the contribution of reaction 5.15, the formation of polyamide radicals by attack of solvent radicals on the nylon chains, would be quite high since the G value for methanol¹⁸ is 14.9 while that for nylon is 5.8. However, a comparison of the concentration of amorphous nylon, ρ , with the concentration of methanol, ρ_s , (in grams per liter of amorphous nylon-styrene-methanol) (Table 5.13) showed the concentration of amorphous nylon was 4.2 - 6.2 fold greater than that of methanol. By using equation 5.8, it was calculated that the rate of initiation of graft polymerization, R_1 , is 1.7-2.4 fold greater than the rate of initiation of homopolymerization, $R_{1,h}$. This difference in the rates of radical formation in

Table 5.13

The Concentration of Amorphous Nylon and Methanol in the System Nylon-Styrene-Methanol

Vol. % styrene in outside solution	(Nylon) $\rho \times 10^{-2}$	(Methanol) $\rho_s \times 10^{-2}$
100	10.6	
90	8.08	1.33
70	7.86	1.52
50	7.72	1.63
30	7.72	1.76
10	7.85	1.94

combination with the competition of styrene monomer for the solvent radicals, reaction 5.16, should make the over-all contribution of reaction 5.15 to the grafting process relatively small.

In the simplified kinetic scheme bimolecular termination was assumed to be exclusively between graft polymer radicals, i.e., reaction 5.3. Other possible modes of bimolecular termination are those of graft polymer radicals with solvent radicals (reaction 5.22) or with homopolymer radicals (reaction 5.23). Termination via reaction 5.22 was deemed relatively unimportant in the nylon-styrene-methanol system due to the same reasons advanced for the unimportance of reaction 5.15.

Although termination via reaction 5.23 is probably quite important, it was ignored in our calculations because it would not qualitatively alter the values of the various calculated terms. That this was the case may be seen by deriving the kinetic equations for bimolecular termination via reaction 5.23. Assuming steady state conditions, one may obtain the following equation in a manner analogous to that employed to obtain equation 5.5.

$$R_1 = 2k_t(PM_n\cdot)^2 + 2k_{t,c}(PM_n\cdot)(M_m\cdot) \quad (5.24)$$

where $k_{t,c}$ = rate constant for cross termination between "inside" homopolymer and graft polymer radicals via reaction 5.23

Similarly, the following equation for the "inside" homopolymerization process (i.e., the homopolymerization which takes place inside the base polymer) may be obtained.

$$R_{1,h} = 2k_{t,h}(M_m\cdot)^2 + 2k_{t,h}(PM_n\cdot)(M_m\cdot) \quad (5.25)$$

acrylate were inhibited with respectfully 0.2% and 0.1% hydroquinone (wt. to vol.). The determinations were made using polymer samples 44 mm. x 14 mm. x 0.050 inch.

Equilibrations of polymer-monomer-solvent systems were carried out in ground glass stoppered test tubes in a constant temperature bath at $25^{\circ} \pm 0.2^{\circ}\text{C}$. until constant weights were obtained. The swollen samples were weighed after wiping them with lint-free absorbent paper. The swollen samples were placed in finely powdered dry ice and irradiated. After irradiation the samples were dried to constant weight under vacuum, the nylon samples at 85°C ., the others at 65°C . and the various calculations were then performed.

6.0 GRAFT POLYMERIZATION VIA IRRADIATION OF RESIN-MONOMER MIXTURES

The major grafting technique used in this work involved swelling the polymer film with monomer until the equilibrium monomer-polymer concentration was reached and then irradiating the swollen film in the presence of excess monomer. Another grafting technique that was used consisted of first mixing the polymer and a fixed amount of monomer at a temperature above the melting point range of the polymer, cooling the resin-monomer mixture to room temperature and then carrying out the irradiation. This method was of great potential industrial interest, since many plastics fabrication operations involve a hot-melt handling step during which a monomer might be readily and inexpensively blended with the polymer.

There were several important differences in the two grafting methods. When hot-melt blending was used, the amount of monomer available was fixed and limited at the beginning of the process. The employment of the technique of hot-melt blending would be limited to monomers which exhibit low vapor pressures at blending temperatures and which are relatively thermally unreactive.

6.1 The Grafting of Vinyl Stearate to Low Density Polyethylene

Vinyl stearate fits this criterion and graft polymers of lowered melt viscosities were prepared from this monomer and low density polyethylene by mixing at elevated

temperatures various amounts of monomer and polymer, then irradiating the cooled mixture to different doses and washing to remove homopolymer. The graft polymers and the conditions by which they were prepared are shown in Table 6.1.

The melt viscosities of the vinyl stearate-polyethylene graft polymers were determined from the measurement of the reaction torques of the samples with a Brabender Plastograph at 125°C. An increase in reaction torque indicated a rise in melt viscosity; a decrease in reaction torque corresponded to a lowering of the melt viscosity. It was found that the addition of vinyl stearate to polyethylene lowered the melt viscosity of the original polymer and that the graft copolymers exhibited lower melt viscosities than mechanical mixtures of polymer and monomer at the same concentration (Table 6.1).

Table 6.1

The Grafting and Melt Viscosity of Vinyl Stearate-Low
Density Polyethylene

Original % vinyl stearate	Dose, Mrads	% Graft	Reaction torque, gram-meters
0	0	0	1450
1	0		1410
	0.21		1390
	0.55	0.12	1200
	1.2	0.64	1180
	3.9		1280
2	0		1380
	1.2		1240
5	0		1280
	0.21	1.4	
	0.55	2.4	1040
	1.2	1.9	1220
	3.9		
10	0		1130
	0.21		
	0.55	3.7	1020
	1.2	5.4	1050
	1.2	3.0	
	3.9	6.8	
20	0		830
	0.21	2.8	940
	0.55	6.0	
	1.2	6.3	

6.2 The Grafting of Allylic Phosphorus Compounds to
Low Density Polyethylene

The graft polymerization of diallyl phosphite and triallyl phosphate to low density polyethylene was investigated using the hot-melt technique. These monomers have high boiling points and homopolymerize slowly below

their boiling points and thus were readily adaptable to this technique. The radiation-induced graft polymerization of these allylic phosphorus compounds with polyethylene appeared promising as it was expected that they would function as crosslinking agents and also impart heat stability to the polyethylene.

The properties of the irradiated monomer-resin mixtures could not be studied since irradiation led to such copious crosslinking that subsequent handling operations were prohibitively difficult. Therefore, the grafting behavior of these systems were determined using thin low density polyethylene films and carrying out the irradiations in the presence of monomer. The heat stabilities of these graft polymer films were then determined and it was shown that the polyethylene film strength was enhanced when the film was irradiated in the presence of the allylic phosphorus compounds. The data and results are in Table 6.2.

Table 6.2

Heat Stability of Low Density Polyethylene Film Grafted
with Allylic Phosphorus Compounds

Monomer	Dose, Mrads	% Graft	Fusion point, °F. (\pm 5°F.)
None	0.0	None	195
	0.091	None	205
	0.23	None	205
	1.3	None	200
	4.6	None	295
Diallyl phosphite	1.3	0.5	190
	2.0	2.2	255
	6.6	2.0	370
Triallyl phosphate	3.2	2.4	350
	5.5	4.7	420

These results showed irradiation of resin-monomer mixtures to be a feasible and practical method by which a series of graft polymers with varying combinations of different desired physical properties could be produced. The success of this work indicated that it should be possible to use this grafting technique in industrial applications that would involve the hot-melt handling of polymers with thermally inactive monomers.

6.3 Experimental

6.3.1 The Grafting of Polyethylene and Vinyl Stearate

Vinyl stearate and low density polyethylene (Alathon 14 Du Pont) were mixed together at 125°C. in a Brabender Plastograph, a constant temperature mixer coupled with a dynamometer-recorder system that measured the reaction torque of the contents of the mixing chamber during the course of the mixing operation. The reaction torque was a

measure of the melt viscosity of the mixture. Monomer-resin mixtures containing 1, 2, 5, 10 and 20 weight percent vinyl stearate were prepared in the Plastograph, and the samples were then irradiated in the RAI Co-60 source to total doses of 0.21 - 3.9 Mrads. The reaction torque of each sample was measured before and after irradiation. After irradiation, the samples were pressed into films in a Carver press at 200°C. This was done so as to accelerate the washing process. The films were soaked in benzene at room temperature for twenty four hours to remove unreacted monomer and homopolymer. It was found that during the pressing operation there was some mechanical loss of material. Therefore, the amount of grafted vinyl stearate was determined by measuring the infrared absorption band at 5.75 μ and 8.55 μ of small samples of pressed films that had been freed of non-grafted stearate.

Since most of the testing procedures require bubble-free film samples of uniform thickness, the test samples were prepared by pressing pure polyethylene and monomer-polyethylene mixtures and then irradiating the pressed films. The percent graft was determined by the infrared absorption method after homopolymer and monomer had been removed.

6.3.2 The Grafting of Polyethylene and Allylic Phosphorus Compounds

Low density polyethylene (Alathon 14 Du Pont) 3 mil films were immersed in the monomers diallyl phosphite and triallyl phosphate and irradiated to various doses in the RAI Co-60 source. For control purposes, another group of films were irradiated to the same doses in the absence of monomer. The films that were irradiated with monomer were soaked in acetone at 60°C. to obtain pure graft polymer. The heat stability was measured by the fusion temperature. This test involved placing the film sample on successively hotter areas of a metal bar whose length spanned a temperature gradient of 0 to 450°F. The temperature at which the film strength decreased so that the film tore on being pulled free of the heated metal was defined as the fusion point.

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